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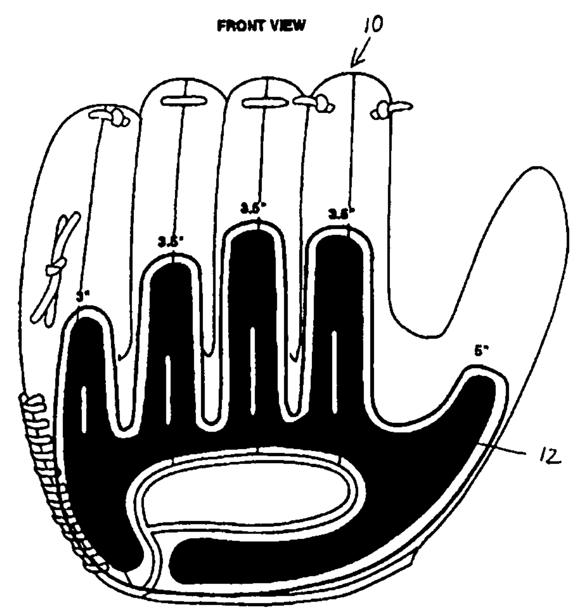
(57) Abstract

The structures include an environmentally responsive gel forming a part of the structure. The gel responds to an environmental condition such as temperature to change state reversibly. It is preferred that the gel be sealed in an enclosure. In one embodiment, the gel is a reverse thermal gel which is liquid at lower temperatures and becomes viscous at body temperatures. Objects placed in contact with the body conform to the body shape and retain the shape in response to body temperature. Representative structures are articles of clothing, such as hats, helmets and brassieres. Other conformable objects include chairs and sofas.

GEL BLADDER FOR CONV... TIONAL FIELDING GLOVE
(12" Glove Bladder)



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CONFORMABLE STRUCTURES

Background of the Invention

This invention relates to conformable structures and more particularly to structures which conform to the body part of a human or animal in response to body heat.

Products which conform to a body part or parts would provide added levels of comfort, support, efficiency and perhaps performance enhancement. Because everyone's body is different, mass produced consumer goods don't fit perfectly. Not only is this the case for wearing apparel and products gripped in the hand, but also objects which come into contact with the body, such as chairs, beds, sofas and other products which support the body. Bladder-based products that conform or provide cushioning are described in United States Patent Nos. 4,144,658 and 5,313,717.

Summary of the Invention

Conformable structures according to the invention include an environmentally-responsive gel forming a part of the structure, the gel responsive to an environmental condition to change state reversibly. The gel may be sealed within an enclosure such as a bladder. The gel may be a crosslinked gel obtainable from a polymeric precursor which is in a gelled state at lower temperatures and contracts to disgorge a liquid at body temperatures. Alternatively, the gel may be a reverse thermal gel which is liquid at lower temperatures and becomes more viscous at body temperatures. The reverse thermal gels include interpenetrating polymer networks containing a responsive component capable of aggregating in response to a change in an environmental stimulus such as temperature, a structural component which supports and interacts with the responsive component, and an aqueous-based solvent. The responsive and structural components may be oligomers or polymers. The responsive component will respond to a stimulus to change its degree of association and/or agglomeration. The

stimulus may be temperature, pH, ionic concentration, solvent concentration, light, magnetic field, electric field, pressure or other triggers commonly used to trigger a responsive gel material. For the application as a conformable structure, temperature is the preferred trigger. The aggregation may be in the form of micelle formation, precipitation, labile crosslinking or other factors.

The structural component is an oligomer or polymer which supports and interacts with the responsive component so that a multi-material, responsive polymer network is formed. The structural component is not required to be responsive. The interaction of the structural and responsive components exhibits a synergistic effect which magnifies the effect of the responsive component in viscosifying and/or gelling the solution. It may also cause a sol-gel transition to occur under conditions which would show no apparent effect in the absence of the polymer network. A typical reversibly gelling polymer network may contain less than about 4 weight percent of total polymer solids of which less than about 2 weight percent is the responsive component and less than about 2 weight percent is the structural component. The rest is made of the aqueous-based solvent. An exemplary responsive component is a triblock polyol having the formula (EO)(PO)(EO). An exemplary structural component is sodium acrylate which is manufactured by polymerization of acrylic acid in the presence of triblock polyol followed by hydration and neutralization of the polyacrylic acid. The viscosity of the gel increases at least ten-fold with an increase in temperature of about 5° C.

Yet another suitable reverse thermal gel is poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) triblock copolymers (trade name Pluronics, Poloxomers) in aqueous solutions. As an aqueous Pluronics solution is heated up, and the temperature exceeds a certain value called a lower transition temperature, the viscosity changes by several orders of magnitude. The consistency of the solution changes from that of a liquid to that of a solid gel (like butter). The particular concentration needed to achieve such a transition depends on the kind of Pluronic polymer. For

example, F127 will not show the gelation properties at concentrations lower than about 16%, whereas other Pluronics may need an even higher concentration.

The materials useful for the inventions disclosed herein may be encapsulated into bladders made of materials suitably impervious to water loss, such as mono- or multi-layered sealable structure of sufficiently low moisture vapor transmission rate to ensure appropriate performance. Suitable materials include, but are not limited to, hydrocarbon-based films, modified hydrocarbon-based films, multi-layered or composite films with both hydrocarbon and metallic-based layers. Additionally, materials such as foams may be adhered to the bladder film for the purpose of making a more effective and stronger material after the gel material undergoes a phase transition. The bladder films may be sealable using heat, pressure, sonic welding, RF and pressure sealing techniques.

The conformable structures of the invention provide improved fit, comfort, mechanical support and shock resistance. Applications may be broken down into the following exemplary categories.

Athletics

The structures may be used for mouthpieces, helmets, head gear (*e.g.*, wrestling), specialty gloves (*e.g.*, baseball, boxing, biking, golf, lacrosse, equestrian, hockey, etc.), masks (*e.g.*, scuba, hockey, soccer, lacrosse, baseball catcher, etc.), goggles (*e.g.*, swimming, skiing, scuba, etc.), lacrosse head stops, sports bras, socks, grips for athletic equipment, ear and nose plugs. Other athletics applications includes grips for oars, tennis, squash and cricket rackets, baseball bats, shoulder pads, knee pads, elbow pads, bicycle handlebars and seats, padding for sleds, saddles and undersaddles, joint support (*e.g.*, elbow, wrist, knee, hip, neck, shoulder and ankle), muscle and bone support, sports clothing including wet suits, dry suits, padded garments (*e.g.*, biking shorts,

etc.), conformable garments and socks. Other uses are for motorcycle grips and gun handles.

Health Care

The conformable structures of the invention may also find application in orthopedic devices, prosthetic appliances, ostomy bag fittings, molding material (dental, etc.), casting, bandaging, joint braces (*e.g.*, elbow, wrist, knee, hip, neck, shoulder and ankle), splints, eyeglass pads and tennis elbow braces. Other health care applications include bedding, bed pads and sheets, whirlpool bath rests, pillows, crutch padding, x-ray boards, walkers, cervical pillows, wheelchair padding, general padding, lumbar supports and electrocardiogram pads.

Office/Furniture

The conformable structures have application in ergodynamic chairs, beds, sofas, shoulder rests and telephone receiver cushioning pads, palm rests for ergonomic keyboards, and other ergonomic computer accessories and cushioning for writing instruments. Other applications are for chairs, seating for vehicles of transport such as automobiles, airplanes, boats, etc., and vibration damping control.

Industrial Applications

Restraints for vehicles of transport, headphones (protective and audio performance), conformable toys (*e.g.*, dolls, sealed tubes containing fluids, and representative models, etc.), valves and actuators, temperature indicators, dog collars, bridles for horses or dogs, and teething rings.

Other industrial applications for the conformable structures include vibration control shock absorbers, socks, shimming, padding for instrumentation, padding for shipping pressure equipment, sealing thermal imaging equipment and oven mitts.

Wearing Apparel

Conformable structures of the invention also have application in brassieres, sports bras, formal dress wear and bathing suits. The materials also may be incorporated into men's jock straps, undershorts or bathing shorts. The material may also be incorporated into an article of eyewear.

Brief Description of the Drawing

Figure 1 is a graph of viscosity versus temperature for a Pluronic material;

Figure 2 is a graph of viscosity versus temperature for another Pluronic material;

Figure 3 is a graph of viscosity versus temperature illustrating the effect of NaCl on transition temperature;

Figure 4(a)-(c) are schematic illustrations of bladders encompassing the conformable structures of the invention; and

Figure 5 is a schematic illustration of a conventional baseball fielder's glove including a gel bladder.

Description of the Preferred Embodiment

In one embodiment, the gel is a microporous, fast response, crosslinked gel obtainable from a polymeric precursor, the gel being reversibly responsive to a change in an environmental condition, preferably temperature. The gel can be made from any responsive polymer with side groups that can react with di- or multi-functional crosslinking molecules. The polymers can have hydroxyl, acid or amine side groups which have lower critical solution temperatures in aqueous solutions together with water-soluble crosslinkers. The precursor is preferably a linear polymer or cellulose ether such as hydroxypropyl acrylate, hydroxyethyl acrylate copolymer. Also, the water-based fluid used to make the gel can include sucrose in the range of 30-60% to vary the reaction temperature.

A temperature-responsive gel suitable for use in the invention is a crosslinked, three-dimensional polymeric network that contains a substantial quantity of liquid so that the properties of the gel are determined by both the polymeric network and the liquid. If the liquid is water, the gel is commonly called a hydrogel. The volume of this type of reactive gel may contract by a factor of up to several hundred percent when the gel undergoes a change in external conditions such as temperature. The network material of a responsive hydrogel may include a number of polymeric materials that possess a lower critical solution temperature (LCST). The term LCST is the temperature below which the polymer is substantially soluble in liquid and above which the polymer is substantially insoluble. Therefore, the responsive gel forms a two phase system. Examples of suitable hydrogels are set forth in U.S. Patent No. 5,183,879, the teachings of which are hereby incorporated by reference. The preferred temperature-responsive gel contracts upon application of heat from contact with the body, thereby causing water to be disgorged from the gel. Therefore, the temperature responsive hydrogel can be enclosed within a bladder to contain water that is expelled from a contracted gel and located in an article of apparel or other structure. The water may then flow around and conform to the portion of the body with which it is in contact. A preferred gel precursor is a linear polymer or cellulose ether, and more particularly, hydroxypropyl acrylate/hydroxyethyl acrylate copolymer. Preferably, the hydroxypropyl acrylate/hydroxyethyl acrylate copolymer gel includes between 50 to 100 percent hydroxypropyl acrylate and between 50 and 0 percent hyroxyethyl acrylate. Further, to enable the temperature-responsive gel to operate at lower temperatures, glycerine or glycerol can be added to reduce the freezing temperature of the solution.

For many applications, it is preferred that the gel material be a reverse thermal gel which is substantially liquid at lower temperatures and whose viscosity increases at body temperatures. One suitable class of materials are

interpenetrating networks of a responsive component such as an oligomer or polymer which will respond to a stimulus to change its degree of association and/or agglomeration. A preferred stimulus is temperature. The aggregation may be in the form of micelle formation, precipitation, labile crosslinking or other factors. The responsive and structural components are dissolved in an aqueous-based solvent. Since a gel comprises three-dimensional polymeric networks dissolved in the solvent, the liquid component makes up a responsive polymer network. Suitable materials are disclosed in detail in pending U.S. Application Serial No. 08/580,986, filed January 3, 1996, the teachings of which are incorporated herein by reference. The following examples are representative of suitable interpenetrating network gels.

Example 1

This example describes the synthesis of a responsive polymer network and an aqueous responsive polymer network solution prepared using a triblock polymer of ethylene oxide and propylene oxide (Pluronic® F27) and poly(acrylic acid). This example also characterizes the gelation and the physical properties of the resultant responsive polymer network.

Synthesis

Block copolymer of propylene oxide (PO) and ethylene oxide (EO) having sandwich structure $(EO)_A(PO)_B(EO)_A$ (Pluronic F127 NF, Poloxamer 407 NF, where "F" means Flakes, "12" means 12X300=3600 - MW of the poly(propylene oxide) section of the block copolymer, "7" ethylene oxide in the copolymer is 70 wt%, and nominal molecular weight is 12,600) from BASF (3.0 g) was dissolved in 3.0 g acrylic acid (Aldrich). This represents a substantially 1:1 molar ratio of Pluronic® F127 and polyacrylic acid. The solution was deaerated by N_2 bubbling for 0.5 h and following addition of 100 μl of freshly prepared saturated solution of ammonium persulfate (Kodak) in deionized water was kept at 70°C for 16h resulting in a transparent polymer.

Viscosity measurements

A known amount of the resultant polymer was suspended in 100 ml deionized water into which NaOH was added. Following swelling for 3 days while stirring, the pH of the resulting fine suspension was adjusted to 7. Samples of 15 ml each were taken, and pH in each vial was adjusted to desired value by addition of 1 M HCl or NaOH. Samples were then kept overnight and their viscosities were measured at different temperatures using Brookfield viscometer using either an SC4-18 or an SC4-25 spindle.

A control experiment was done with a physical blend of Pluronic® F127 and polyacrylic acid (MW 450,000) available from Aldrich. Pluronic® F127 and polyacrylic acid were dissolved together in deionized water at 1 wt% total polymer concentration and the resultant solution was adjusted to pH 7, stirred and kept in refrigerator.

It was generally observed that 1-5 wt% responsive polymer network compositions made of Pluronic® F127 and polyacrylic acid viscosify at temperatures of around 30° C and higher if pH is adjusted to 6 or higher. The gelling effect was observed in responsive polymer network compositions standing 3 months or longer. Repeated heating and cooling of responsive polymer network compositions did not cause deterioration of the responsive polymer network or the gelling effect. Solutions of either Pluronic F127 or polyacrylic acid (1-5 w% in water, adjusted to pH 6 or higher) or physical blends of the two lacked the gelling effects found for responsive polymer network compositions.

Responsive polymer network structure

Solutions (1 wt% each) of responsive polymer network composition, a polyacrylic acid (alone) polymerized without Pluronic® and Pluronic® F127 (alone) were subjected to gel permeation chromatography analysis using triple detector system (light scattering, viscometer, and refractive index detection, Viscotek). The results of molecular weight determination are outlined in Table 1.

Table 1. Results of molecular weight determination of polyacrylic acid in responsive polymer network, polyacrylic acid itself (PAA), and Pluronic F127.

Parameter	Definition	responsive polymer network complex	polyacrylic acid	Pluronic F127
Number-average MW	$M_n = \Sigma n_i M_i / \Sigma n_i$	212,200	782,000	12,100
Weight-average MW	$M_w = \Sigma n_i M_i^2 / \Sigma n_i$	391,100	3,096,000	12,500
z-Average	$M_z = \Sigma n_i M_i^3 / \Sigma n_i M_i^2$	775,600	14,620,000	12,900
Peak average	determined by MW standards	297,000	1,140,000	-
Polydispersity	M_w/M_n	1.84	3.96	1.03
Radius of gyration	rms distance from mass center	17.51	62.14	4.34

It can be seen from Table 1 that polyacrylic acid of the responsive polymer network composition and polyacrylic acid synthesized alone are substantially different in molecular weights and polydispersity. The presence of the triblock (EO)(PO)(EO) polymer and its interaction with the developing polyacrylic acid chains had a measurable effect on the final responsive polymer network composition. Namely, polyacrylic acid synthesized in presence of the triblock (EO)(PO)(EO) polymer is of lower molecular weight and is much more monodisperse than the polyacrylic acid prepared alone. Pluronic® was very monodisperse and it's molecular weight corresponded to the data provided by the supplier. Thus, the responsive polymer network compositions of the present invention are more than the sum of two individual polymers.

Further information on the structure of the responsive polymer network may be gained using the Mark-Houwink equation. Analysis using Mark-Houwink equation

$$[\eta] = K\, M_v^{a}, \tag{1}$$

where $[\eta]$ is intrinsic viscosity of (dilute) polymer solution, M_v is viscosity-average molecular weight of the polymer, K and a are specific constants, can reveal the status of the polymeric chains. The viscosity and molecular weight

data obtained for PAA and responsive polymer network are expressed in terms of equation (1), in double logarithmic coordinates so that the initial slope of the curves corresponds to the parameter *a*, which is a measure of branching of the polymeric chains. Results on measurement of *a* are collected in Table 2.

Table 2. Mark-Houwink parameter *a* and it's interpretation.

System	*a*	Interpretation
Dilute polymer solution in a good solvent	≈ 0.5	Random coil
Same	≈ 1.8	Rigid rod
1 wt% polyacrylic acid	0.477 (Log K = -1.990)	Linear
1 wt% responsive polymer network composition	1.212 (LogK = -6.646)	Highly branched
1 wt% Pluronic® F127	0.529 (Log K = -2.907)	Linear

Comparison of *a* values suggests that polyacrylic acid prepared by itself and Pluronic® F127 are linear, whereas the responsive polymer network composition is highly branched (see differences in *a* and K). Because the preparation of the responsive polymer network composition uses preformed triblock polymer, it may be reasonably assumed that the polyacrylic acid of the responsive polymer network composition is the source of the branching.

Branching of polyacrylic acid in the responsive polymer network composition can explain its stability (i.e. ability of responsive polymer network composition to remain thermo-responsive in dilute solutions for many months). Branched polyacrylic acid molecules interpenetrate and become entangled with each other and with the triblock (EO)(PO)(EO) polymer and thereby forms a constrained, stable structure. Because of the branching nature of the polyacrylic acid in the responsive polymer network composition and the degree of entanglement which arises from the preparation of the interacting network, the constituent polymers experience a much stronger degree of interaction than physically mixed polymers. These structures interact even more strongly because of the tendency of responsive

components, such as the triblock (EO)(PO)(EO) polymers to form aggregates in solution. No covalent bonds, i.e., crosslinks, are even required for either of the constituent polymers.

The following set of experiments was carried out to establish absence of covalent bonds between Pluronic® and polyacrylic acid in the responsive polymer network compositions. Responsive polymer network compositions made of Pluronic® F127 and polyacrylic acid (1 g), in dry state, were stored in excess methylene chloride (350 ml) for 2 weeks, where it swelled greatly. Non-dissolved part of the responsive polymer network was removed from the solvent and dried. The solvent was dried to obtain white flakes of the soluble component of the responsive polymer network. The flakes were analyzed by Fourier Transform IR (FTIR) and its spectrum was found to correspond to the spectrum of Pluronic® F127. The insoluble portion of the responsive polymer network was analyzed by FTIR and compared to a sample of pure polyacrylic acid (MW 450,000, from Aldrich). The polyacrylic acid extracted from responsive polymer network and the one available commercially were spectroscopically identical. Thus, the individual components of the responsive polymer network may be separated by solvent extraction, indicating the lack of covalent bonding. Thus, the responsive polymer network composition described above is a unique composition of matter consisting of interacting and entangled polyacrylic acid and copolymers of ethylene oxide and propylene oxide (Pluronic®), without covalent bonding.

Example 2

This example describes the synthesis of a responsive polymer network and an aqueous responsive polymer network composition prepared using Pluronic® F108 and poly(acrylic acid). This example also characterizes the gelation and the physical properties of the resultant responsive polymer network composition.

Synthesis

Block copolymer of propylene oxide (PO) and ethylene oxide (EO) having sandwich structure $(EO)_A(PO)_B(EO)_A$ (Pluronic F108 NF, Poloxamer 338 NF, where "F" means Flakes, "10" means 10X300=3000 - MW of the poly(propylene oxide) section of the block copolymer, "8" means that the weight percentage of ethylene oxide in the copolymer is 80%, and nominal molecular weight is 14,600, 3.0 g) was dissolved in 3.0 g acrylic acid (Aldrich). The solution was prepared as described above for Example 1.

Viscosity measurements

A known amount of the resultant polymer was suspended in 100 ml deionized water into which NaOH was added. Following swelling for 3 days while stirring, the pH of the resulting fine suspension was adjusted to 7. The responsive polymer network composition was studied as described in Example 1. Responsive polymer network compositions of 1 wt% Pluronic® F108 and polyacrylic acid (1:1) viscosified at temperatures of around 34°C and higher at pH 7. Repeated heating and cooling of the responsive polymer network composition did not degrade the gelling effect. The liquid to gel transition of 34°C correlates well with the observed characteristic temperature of 33.7°C of the endothermic peaks that are seen in the DSC endotherm. The peaks are measured to have enthalpy value of 1.504 cal/g. This also corresponds closely to a similar endotherm observed for Pluronic® F108 alone. The observed correlation supports the conclusion that it is the formation of the triblock (EO)(PO)(EO) polymer aggregates that contribute to the gelation of the responsive polymer network compositions.

Example 3

This example describes the synthesis of a responsive polymer network and an aqueous responsive polymer network composition prepared using Pluronic®F88 Prill and poly(acrylic acid). This example also characterizes the

gelation and the physical properties of the resultant responsive polymer network composition.

Synthesis

Block copolymer of propylene oxide (PO) and ethylene oxide (EO) having sandwich structure $(EO)_A(PO)_B(EO)_A$ (Pluronic F88 Prill, where "F" means Flakes, "8" means 8X300=2400 - MW of the poly(propylene oxide) section of the block copolymer, "8" means 80 wt% ethylene oxide in the copolymer is 80%, and the nominal molecular weight is 11,400, 3.0 g) was dissolved in 3.0 g acrylic acid (Aldrich). The solution was prepared as described above for Example 1.

Viscosity measurements

A responsive polymer network composition was prepared and studied as described in Example 1. Responsive polymer network compositions of 1 wt% Pluronic® F88 and polyacrylic acid (1:1) viscossified at temperatures of around 48° C and higher at pH 7. Repeated heating and cooling of responsive polymer network suspensions was not observed to cause deterioration of the gelation effect. This measurement correlates well with the observed characteristic temperature of 47° C of the endothermic peaks that are seen in the DSC endotherm. The peaks are measured to have enthalpy value of 0.9 cal/g.

Pluronic polyols are also suitable for use in the conformable structures of the invention. Poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) triblock copolymers (trade name Pluronics, Poloxamers) in aqueous solutions show some remarkable reverse thermoviscossification properties.

As an aqueous Pluronic solution is heated up and the temperature exceeds a certain value, called here the lower transition temperature, the viscosity changes by several orders of magnitude. The consistency of the solution changes from that of a liquid to that of a solid gel (like butter). The particular concentration needed to achieve such a transition depends on the kind of Pluronic polymer. For example, F127 will not show the gelation

properties at concentrations lower than about 16%, whereas other Pluronics may need an even higher concentration. Figure 1 illustrates the viscossification of 17% aqueous solution of F127. It also shows that the viscosity can be increased by adding a thickener, in this case 1% of hydroxyethylcellulose.

Another potentially desirable property of a Pluronic solution is that when the gel temperature is further increased, it can revert to a liquid state. This is useful, for example, in connection with conformable products, where there is a need to distinguish between the effect of contact with human body temperatures, when the materials should be a gel, and a potentially higher ambient temperature (e.g., in a car trunk on a hot day), when the material should be a liquid. Figure 2 shows this effect for a 17% solution of F127, both for increasing and for decreasing temperature.

For may potential uses of the material it is desirable to be able to control the exact transition temperature. This can be achieved by varying the Pluronic type, as well as the concentration of a given Pluronic solution. A straightforward way of controlling the temperature is by modifying a solution of given concentration through incorporation of additives, such as salts and polymers. Figure 3 shows the effect of addition of sodium chloride to a 30% solution of Pluronic F68. The transition temperature can be brought down from 45°C to 10°C by addition of 10% (by weight) of NaCl.

An increase in the material strength as it changes from a liquid to a gel is significant, but it may not be sufficient for some applications. An appropriate system may be designed to augment the strength. Figure 4a illustrates a cross-section of a bladder filled with a Pluronic solution. As the material thermoviscosifies the bladder becomes harder. The resistance to flow in this design is not very great. It can be improved by incorporation of a foam into the bladder, as illustrated in Figure 4b. The foam is impregnated with the Pluronic solution and provides a resistance to flow. When the material thermoviscosifies, the resistance becomes much greater, and the foam

becomes very hard and rigid. Another structural design improving the strength of the viscosified material is presented in Figure 4c. The bladder is divided into a number of chambers (two are depicted here) separated by narrow channels, through which the Pluronic solution must flow in order to redistribute itself when pressed or squeezed. When the solution viscossifies, the resistance to flow offered by these narrow channels is much greater than that in the case of an open bladder, as in Figure 4a. Therefore the overall stiffness of the systems is enhanced.

In order to further enhance the usefulness of the Pluronic solution to its application in consumer products, a thermochromatic dye can be incorporated into the solution and/or the bladder or container. The user's perception of a radical change in the material properties is then enhanced by a change in the material's color.

In particular, a thermochromatic material is commercially available from 2nd Story Concepts, Inc. When suspended in an aqueous solution, it is capable of changing color from its original hue at low temperatures to white at body temperature. The thermochromatic powder may be incorporated either directly into the bulk of the gel or into the structure of the container holding the gel. Further colors can be achieved by mixing the thermochromatic powder with a dye of desired color to the effect that at high temperatures the color is that of the dye and at low temperature the color is determined by the composition of the dye color with the basic hue of the thermochromatic powder. As an example, a 50/50 mixture of 10% gel solution in 1% suspension of the thermochromatic powder was prepared. A blue to white change in color accompanied the reverse thermal gelation of the systems. Different color changes were achieved by incorporating dyes into the system, for example, purple to red, green to yellow.

It is preferred that the gel materials of the invention be encapsulated within bladders. Bladder materials will consist of a mono or multilayered

sealable structure of sufficient MVTR (Moisture Vapor Transmission Rate) to ensure product performance over the lifetime of the product.

Some examples include, but are not limited to, hydrocarbon based films, modified hydrocarbon based films, multilayered or composite films with both hydrocarbon and metallic based layers.

Additionally, materials such as foams and the like may be adhered to the film for the purpose of making a more effective (*i.e.*, stronger) material after the phase transition.

Films may be sealable using heat/pressure, sonic welding, RF and pressure adhesive sealing techniques. Additionally, vacuum and heat forming of the package may be required.

Bladder Manufacturing

The bladder may be manufactured using one of three basic techniques. 1) form, fill and seal, and 2) vacuum form, fill and seal, and 3) pouch prefabrication, fill and seal. Form, fill and seal utilizes the formation of the pouch while at the same time the pouch is filled with the responsive polymer network material.

Vacuum form, fill and seal utilizes a vacuum forming step prior to the filling and sealing operations. The bladder material must be somewhat thicker than the form fill and seal case in that the material will thin out and weaken at the corners being formed. The hollow that has been formed can be filled with a liquid, or a combination of liquids and solids in one or sequential steps.

Pouch prefabrication, fill and seal utilizes a premade pouch that is filled with liquids and/or solids in a subsequent filling step and then sealed. Variations of this technique may include filling a premade rigid or soft pouch and then sealing or filling a soft pouch utilizing one way valves that are subsequently cut off and sealed.

With reference now to Figure 5, a baseball fielder's glove 10 includes a gel bladder 12 disposed as shown in the figure. It is preferred that the gel within the gel bladder 12 be either the interpenetrating network gel or the Pluronic gel described above. When a hand is inserted into the glove 10, the gel is in the liquid state and conforms to the hand of the wearer (not shown). As the gel warms to body temperature, it becomes viscous, thereby retaining its shape and conforming to the hand of the wearer.

It will be readily apparent to those skilled in the art that the gel bladders of the invention may be incorporated into any of the articles of clothing or other articles of manufacture set forth earlier in this specification. In all of these applications the gel undergoes a phase change or transition from a first state at a lower temperature to a second state at body temperature. In the case of reverse thermal gels, the gel at the lower temperature is liquid and becomes viscous upon contact with the body.

Claims

1. Conformable structure comprising:

an environmentally responsive gel forming a part of the structure, the gel responsive to an environmental condition to change state reversibly.

2. The structure of claim 1 wherein the gel is sealed within an enclosure.

3. The structure of claim 1 wherein the gel is a crosslinked gel obtainable from a polymeric precursor.

4. The structure of claim 1 wherein the gel is a interpenetrating network gel.

5. The structure of claim 1 wherein the gel is a Pluronic based gel.

6. A system for providing comfortably mechanical support to a portion of the human body comprising a thermally responsive polymer contained in a polymer membrane of limited water permeability and located to be exposed to human temperature, said thermally responsive gel adapted to be fluid below local body temperature and further adapted to increase in viscosity to provide support when exposed to the temperature of the human body as measured at the point at which the gel is disposed.

7. The system of claim 6 wherein the responsive gel is included within a glove or sporting mitt.

8. The system of claim 6 wherein the responsive gel is worn on or in the ear.

9. The system of claim 6 wherein the responsive gel is adapted to provide improved audio responsiveness by conformable fit in the inner ear.

10. The system of claim 6 wherein the responsive gel is incorporated into a bicycle seat.

11. The system of claim 6 wherein the responsive gel is incorporated into a toilet seat.

12. The system of claim 6 wherein the responsive gel is incorporated into a helmet, cap or other piece of headgear.

13. The system of claim 6 wherein the responsive gel is incorporated into handles.

14. The system of claim 6 wherein the responsive gel is incorporated into a face mask.

15. The system of claim 6 wherein the responsive gel is incorporated into goggles.

16. The system of claim 6 wherein the responsive gel is incorporated into a mouthpiece.

17. The system of claim 6 wherein the responsive gel is incorporated in a medical device.

18. The system of claim 6 wherein the responsive gel provides an orthotic.

19. The system of claim 6 wherein the responsive gel functions as part of a splint, cast or brace.

20. The system of claim 6 wherein the responsive gel is incorporated into an article of protective padding.

21. The system of claim 6 wherein the responsive gel is incorporated into a bed sheet, mattress and paramedics board.

22. The system of claim 6 wherein the responsive gel is incorporated into a chair.

23. The system of claim 6 wherein the responsive gel is incorporated into an article of clothing to provide support.

24. The system of claim 6 wherein the responsive gel is incorporated into a brassiere, sports bra, formal dress wear or bathing suit.

25. The system of claim 6 wherein the responsive gel is incorporated into men's jock strap, undershorts or bathing shorts.

26. The system of claim 6 wherein the responsive gel is incorporated into an article of eyewear.

27. The system of claim 6 wherein the responsive gel is incorporated into a toy.

28. The system of claim 6 wherein the responsive gel is incorporated into a teething ring.

29. The system of claim 6 wherein the bladder membrane is designed to allow permeation of no more than one percent of the fluid over a two year period.

30. The system of claim 6 wherein the bladder membrane is designed to allow permeation of no more than one percent of the fluid over a six month period.

31. The system of claim 6 wherein the gel is designed so that permeation of up to ten percent of the fluid will not change substantially the thermal viscossification temperature or properties.

32. The system of claim 6 wherein the gel is impregnated into a foam.

33. The system of claim 6 wherein the gel contains a thermochromic material.

34. The system of claim 6 wherein the gel contains solutes designed to change the thermal or viscosity properties of the gel.

35. The system of claim 6 wherein the gel contains an antifreeze designed to prevent freezing or boiling at naturally occurring conditions from -25° F to +155° F.

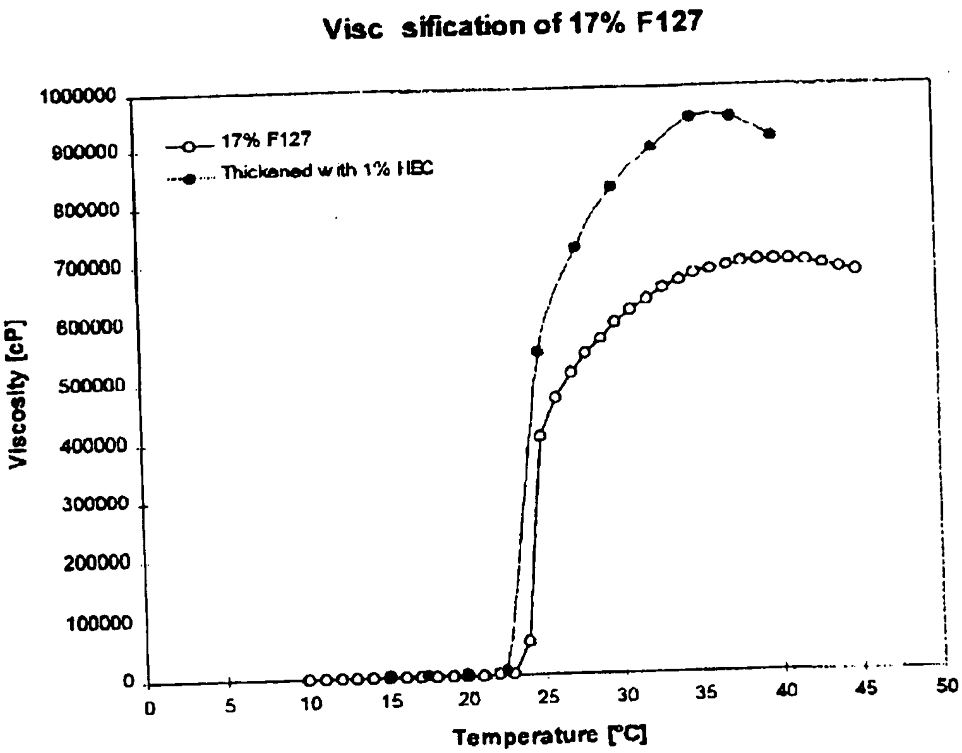


Figure 1 Thermoviscosification curve of 17% Pluronic F127, and 17% F127 thickened with 1% Hydroxyethyl Cellulose (Brookfield viscometer RVDV-II+, 1rpm, spindle #7)

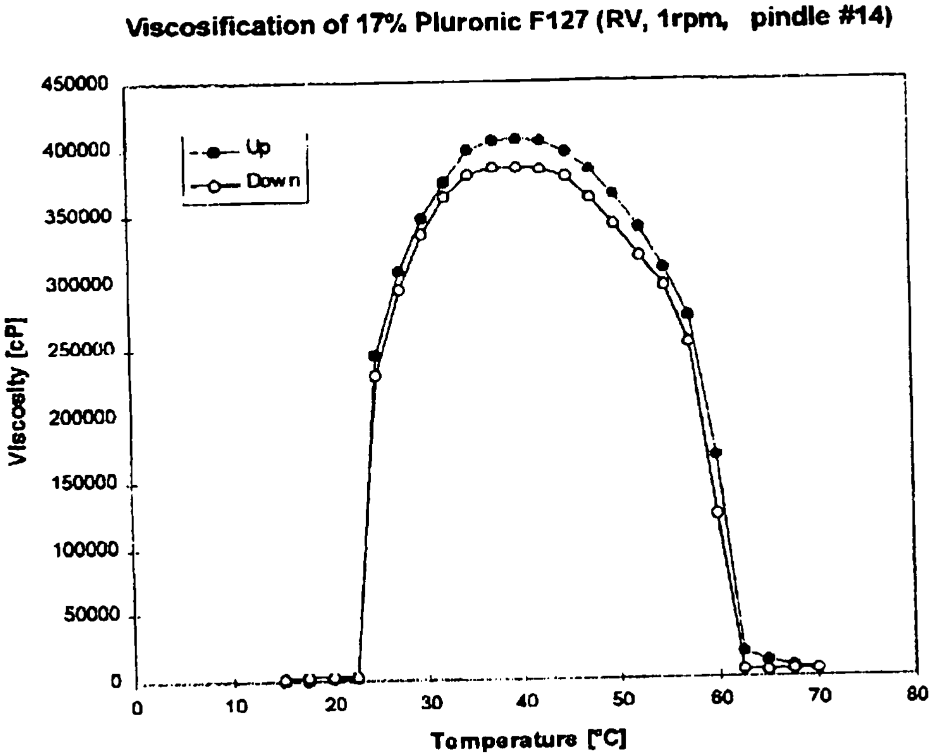


Figure 2: Viscosification of 17% Pluronic F127 (Brookfield viscometer RVDV-II+, 1rpm, spindle #14)

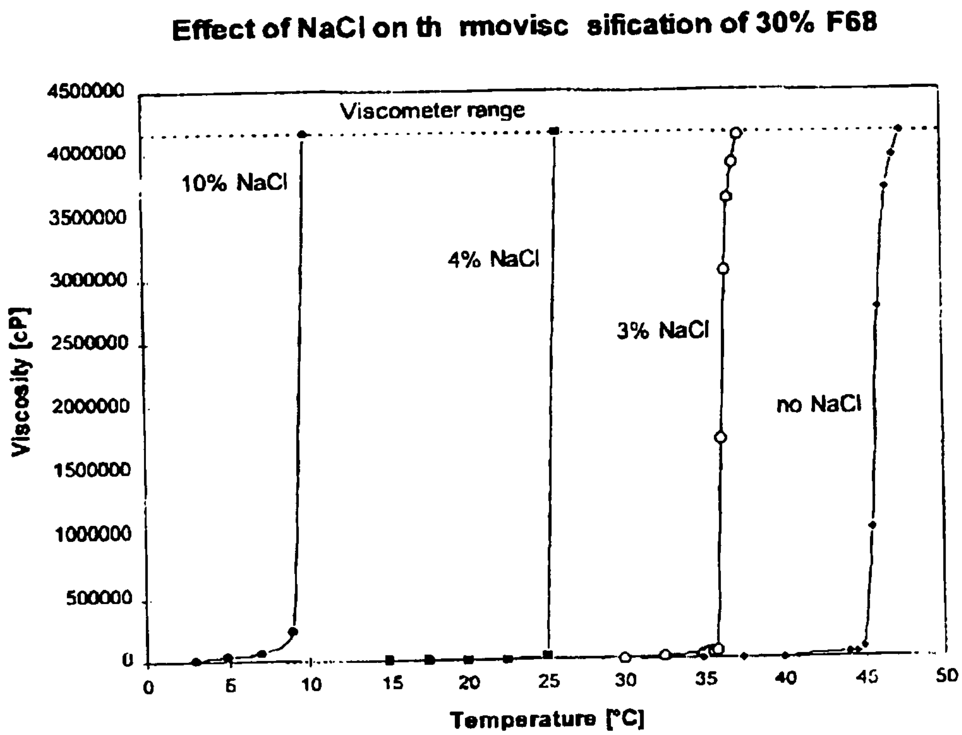
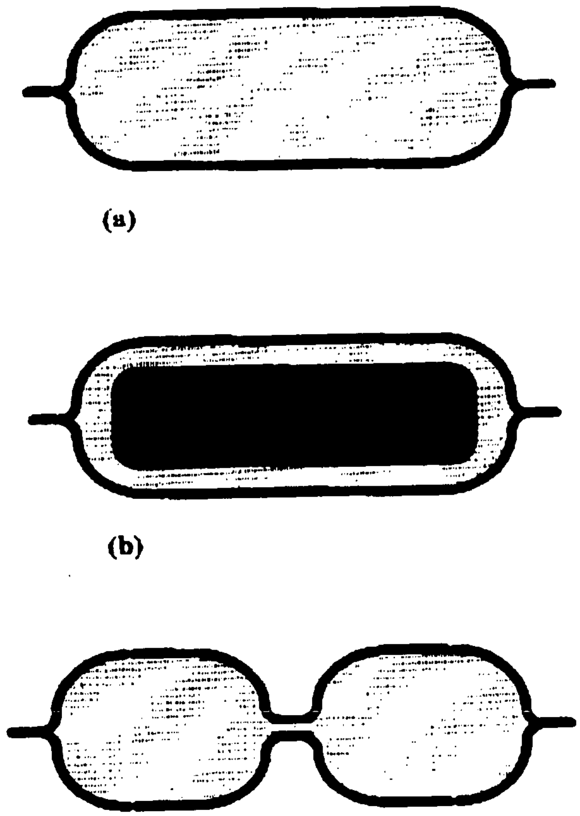


Figure 3 Effect of NaCl on the transition temperature of 30% Pluronic F68 (Brookfield viscometer RVDV-II+, 0.3rpm, spindle #14)



(a)

(b)

(c)

Figure 4

FRONT VIEW

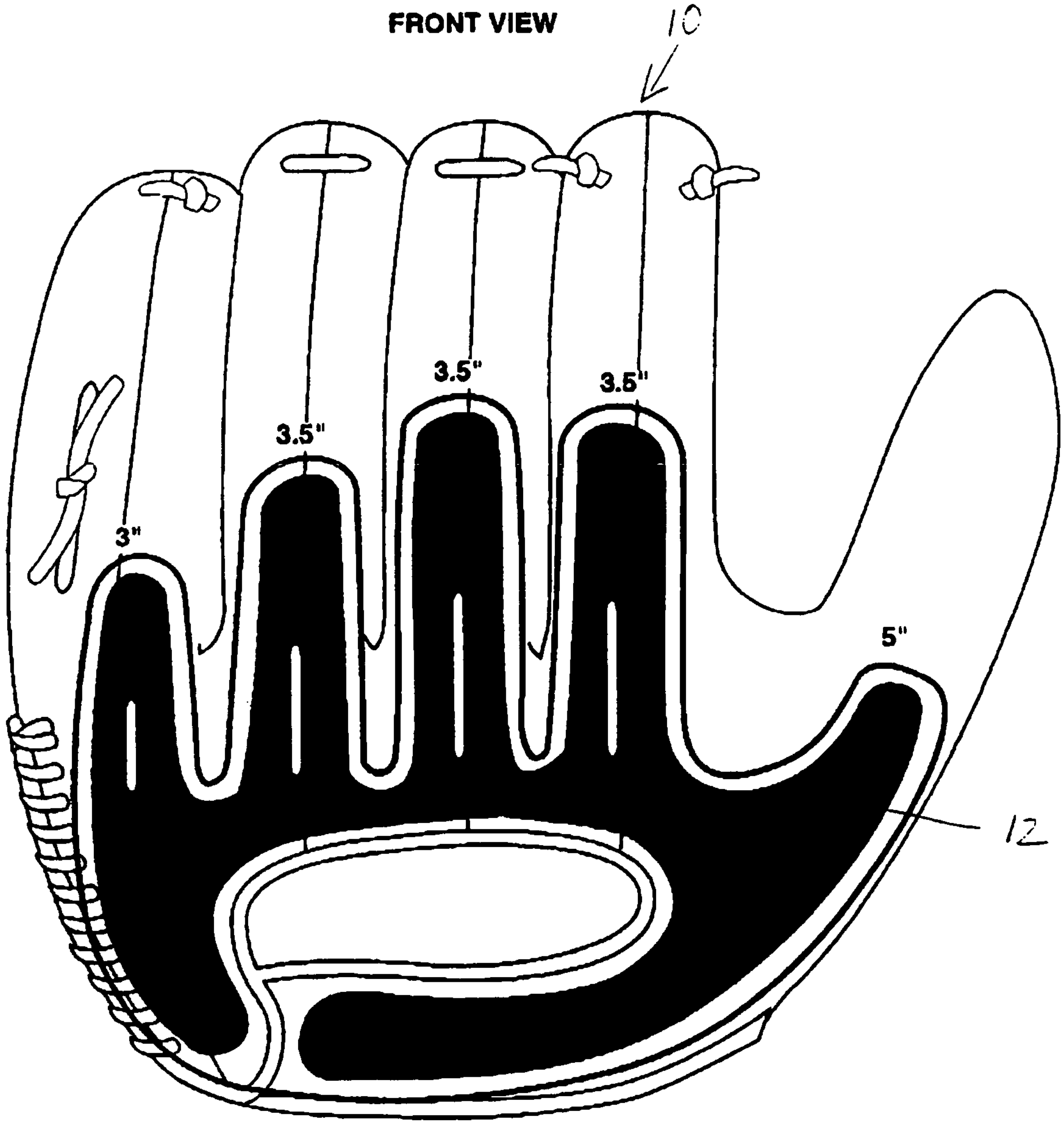


FIG. 5 CONVENTIONAL MODEL

INTERNATIONAL SEARCH REPORT

Inter nal Application No
PCT/US 96/03470

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 A43B7/28 A41D13/10 A47C27/00 A61F15/00 A61G7/00
A42B3/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 A43B A61L A47C A61F A41D A61G A42B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	see the whole document	6-28,32, 34
	see specially (scope-related): see column 3, line 3 - column 5, line 20 see column 6, line 23 - column 7, line 17 see column 7, line 42 - line 47 see claims 1-4,6-8 see very specially claim 7 ---	
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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
10 July 1996	19.07.96
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax (+ 31-70) 340-3016	Authorized officer Molto Pinol, F

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